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(19)



## (54) PROCESS FOR PREPARATION OF A PIGMENT DISPERSED COMPOSITION

(71) We, NIPPON PAINT CO., LTD., a joint-stock company organised under the laws of Japan, of No.2-1-1, Oyodo-cho Kita-Oyodo-ku, Osaka-shi, Osaka-fu, Japan, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:

The present invention relates to a process for the preparation of a pigment dispersed composition.

As an advantageous method for preparation of a composition comprising a resin and a pigment dispersed therein, there is known a process which comprises subjecting a composition comprising a pigment, polymerizable monomers and a resin to suspension or bulk polymerization (United Kingdom Patent Application No. 1,450,941). The composition obtained by this known process can be advantageously employed for the colouring and colour matching of coating materials, particularly for the preparation, colouring and colour matching of powdery paints. When suspension polymerization is adopted in this known process, the adsorption of the resin on to the surface of the pigment is sometimes insufficient depending on the amount and the kind of the resin in the starting composition and the kind of the pigment to be combined therewith. In such a case, recoagulation of the pigment in the dispersed particles is readily caused, and, besides, the pigment shows a tendency to move into the aqueous phase rather than to be retained in the dispersed particles. In addition, the polymerization is effected in an aqueous system so that the adsorption of water on to the surface of the pigment is apt to occur in the case of using a hydrophilic pigment, which may be disadvantageous in respect of the removal of water and drying.

Under such conditions, surface deficiencies are often produced. It is thus difficult to prevent the production of surface deficiencies (e.g. insufficient gloss) in the coating film obtained by the use of such a pigment composition. When bulk polymerization is adopted in the latter proposal, on the other hand, a dispersed state of the pigment can be maintained by stirring which subjects the pigment to shearing forces, and removal of water adsorbed on to the pigment is attained by the reaction heat, which would result in a prevention of the production of surface deficiencies in the formed coating film as seen in the composition obtained by suspension polymerization. However, bulk polymerization is usually carried out at a higher reaction temperature than that of suspension or emulsion polymerization. Therefore, in the case of a starting composition comprising such components as cause cross-linking, gelation or other side-reactions at the said reaction temperature in addition to the designed polymerization reaction, a desired composition suitable for powder coating is difficult or impossible to obtain. Besides, control of the reaction temperature and attainment of a high conversion in polymerization are extremely difficult.

An object of the present invention is to overcome the drawbacks mentioned above. A particular feature of the invention is that a composition comprising a pigment and polymerizable monomers with or without a resin is first subjected to bulk polymerization and then to suspension or emulsion polymerization. Thus, a pigment is blended from the beginning in the starting composition, which is subjected to bulk polymerization. In the bulk polymerization, the pigment is completely wetted with polymerizable monomers, and the polymerization proceeds on the surface of the pigment so that the pigment dispersed in the resulting

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composition is very stable and would not coagulate in the subsequent suspension or emulsion polymerization. Therefore, the coating film formed by the use of the resulting pigment dispersed composition has better smoothness and appearance than that formed by the use of a pigment dispersed composition prepared by the said known process. In the process of this invention, the amount of the starting resin for dispersion of the pigment can be reduced, and in some cases, the use of the resin can be omitted. Further, the kind of the resin may be optionally chosen from a wide range. Besides water adsorbed on to the surface of the pigment can be removed, which resulted in a solution of the problem of a bad influence on the fluidity and the gloss of the coating film. In addition, control of the reaction is easy because suspension or emulsion polymerization is carried out after bulk polymerization. In the case of starting materials which may cause undesirable side-reactions such as cross-linking, their addition may be effected without disadvantages before, or in the course of, the suspension of emulsion polymerization which is usually carried out at a low temperature of 100°C or less.

Accordingly, the present invention provides a process for preparing a pigment-dispersed composition wherein a liquid composition comprising at least one ethylenically unsaturated, polymerizable liquid monomer and at least one pigment in a particulate form dispersed therein in an amount of not more than 70% by weight of the pigment based on the weight of the liquid composition, is subjected to bulk polymerization without cross-linking in a substantially non-aqueous system at a temperature of from 60 to 160°C and wherein, thereafter, the resulting reaction mixture optionally after the addition thereto of a further amount of the said liquid monomer or other ethylenically unsaturated, polymerizable liquid monomer is subjected either to suspension polymerization in an aqueous system at a temperature of from 50°C to 100°C or to emulsion polymerization in an aqueous system at a temperature of 0°C to 100°C to obtain a dispersion of the pigment particles in the polymer particles produced from the liquid monomer or monomers.

In the context of the present invention the adjective "liquid" used to describe the composition and the monomer means liquid at NTP.

In general, bulk polymerisation is carried out in the presence of a conventional polymerisation catalyst and the subsequent suspension or emulsion polymerisation is also effected in the presence of a conventional polymerisation catalyst and in the presence of a suspending agent or an emulsifier.

Before or after or in the course of the dispersion, a further amount of the polymerisable monomer or of a further polymerizable monomer, a resin, a cross-linking agent and/or other additives may be added to the reaction system, if desired.

As the pigment, there may be used a conventional pigment for paints, inks or plastics. Specific examples are inorganic pigments such as substances mainly consisting of an element alone (e.g. carbon black or aluminium powder) and oxides, sulfates, sulfides, chromates, silicates, hydroxides and carbonates of metals such as Zn, Pb, Ti, Sb, Cd, Fe, As, Mg, Al, Ba, Ca, Si, Co and Cr, and organic pigments such as natural dyes, nitroso pigments, nitro pigments, phthalocyanine pigments, basic dyes, acidic dyes, vat dyes, mordant dyes, quinacridone red, quinacridone violet, perylene red, perylene scarlet, isoindolinone yellow, dioxazine violet, aniline black and organic fluorescent pigments. There may also be employed so-called "coated pigments" obtained by coating such pigments as mentioned above with rosin esters or vinyl resins. The amount of the pigment used is not larger than 70% by weight on the basis of the total amount of the starting composition. When the amount is larger, handling may become difficult owing to an increase in the viscosity. As regards the lower limit, there is no particular limitation, and usually it may be not less than 1% by weight. In the choice of the pigment to be used, it is favourably taken into consideration that the pigment does not cause any undesirable side-reaction with other components, i.e. the polymerizable monomer, the resin and the like during the polymerization.

The liquid polymerizable monomer to be used in the invention may be any conventional one. For giving desirable properties to the desired pigment dispersed composition, two or more kinds may be employed. Specific examples of such monomers are styrene,  $\alpha$ -methylstyrene, vinyltoluene, *p*-tert-butylstyrene, vinyl acetate, vinyl propionate, acrylonitrile, methacrylonitrile, 2-hydroxyethyl acrylate, 2-hydroxypropyl acrylate, 1-methyl-2-hydroxyethyl acrylate, 2-hydroxyethyl methacrylate, 2-hydroxypropylmethacrylate, 1-methyl-2-hydroxyethyl methacrylate, acrylamide, N-methylolacrylamide, N-alkoxymethylacrylamide (having 1 to 15 carbon atoms in the alkyl group), acrylic acid, methacrylic acid, esters of acrylic or methacrylic acid with alcohols having an alkyl group of 1 to 15 carbon atoms, crotonic acid, itaconic acid, fumaric acid, dibutyl fumarate, maleic anhydride, monobutyl maleate, methoxyethyl acrylate, ethoxyethyl acrylate, butoxyethyl acrylate, glycidyl acrylate, glycidyl methacrylate,

addition products of glycidyl acrylate or methacrylate with fatty acids, vinylpyrrolidone, vinylpyridine, vinylimidazole, N,N'-dimethylaminoethyl methacrylate, divinylbenzene, diallyl phthalate, triallyl isocyanurate and polyethylene glycol dimethacrylate.

The liquid composition may optionally comprise at least one resin dissolved or dispersed in the liquid monomer. As the resin, there may be used a resin which can be dissolved or dispersed in the said polymerizable monomer. Examples of such resins are natural resins, rosin esters, cellulose derivatives such as cellulose acetate, cellulose acetate butyrate, cellulose acetate propionate, ethyl-cellulose and methylcellulose, vinyl resin with or without a functional group in the molecule, petrolueum resins, phenol resins, urea resins, melamine resins, epoxy resins, silicone resins, urethane resins, xylene resins, toluene resins, alkyd resins, etc. More favourably, these resins may contain in the molecule a so-called "graftable site" such as a polymerizable unsaturated group, a mercapto group or a group capable of causing the abstraction of hydrogen by a free radical. One or more kinds of these resins are preferably incorporated into the starting composition to be subjected to bulk polymerization, in particular, in order to assist the polymerizable monomers with wetting of the pigment. In such a case, the amount of the resin to be used may be not larger than 60% by weight on the basis of the total amount of the starting composition. As regards the lower limit, there is no particular restriction, and it may be ordinarily not less than 1% by weight. In particular in the case of a resin containing in its molecule a graftable site and which is copolymerizable with the polymerizable monomers, graft copolymerization with them is effected on the surface of the pigment dispersed stably by the said resin, so that a sufficiently stable pigment dispersed composition can be obtained, recoagulation of the pigment at suspension or emulsion polymerization being prevented.

Among the polymerizable monomers and the resins mentioned above, monomers containing no cross-linkable functional group (e.g. styrene,  $\alpha$ -methylstyrene, vinyl acetate or esters of acrylic or methacrylic acid with alcohols), natural resins, the usual cellulose derivatives, vinyl resins containing no functional group in the molecule, alkyd resins containing no polymerizable unsaturated group in the molecule and resins containing in the molecule no graftable site may be incorporated at either one of the bulk polymerization and the suspension or emulsion polymerization stages, or at both of them.

As regards monomers containing a cross-linkable functional group such as hydroxyl group-containing monomers (e.g. 2-hydroxyethyl acrylate), acids and acid anhydrides such as crotonic acid, itaconic acid and maleic anhydride, methoxyethyl acrylate and epoxy group-containing monomers such as glycidyl methacrylate, polymers containing a functional group derived therefrom, vinyl resins containing a functional group in the molecule, alkyd resins containing a functional group in the molecule, melamine resins, epoxy resins and the like, two or more kinds of them being cross-linkable between them should not be incorporated at the same time at the bulk polymerization, and at least one of them should be incorporated at the suspension or emulsion polymerization so as to prevent side-reactions such as cross-linking.

Those which are soluble in, or miscible with, water, for instance, monomers containing a carboxyl group, a hydroxyl group, an ether group, a methyl group or an alkoxymethyl group, are taken into the structure of the polymer when incorporated at the bulk polymerization stage, so that movement into the aqueous phase at the suspension or emulsion polymerization stage can be advantageously prevented or minimized.

In the case of the incorporation of a so-called cross-linking agent such as a melamine resin, a blocked polyisocyanate or a polybasic acid or an acid anhydride such as sebacic acid, 1,10-decanedicarboxylic acid, phthalic anhydride or trimellitic acid anhydride at the polymerization stage, the same care as mentioned above should be taken in the combination of two or more kinds of the said polymerizable monomers or resins which are crosslinkable between them so as to prevent undesirable side-reactions such as cross-linking.

The dispersing treatment of the starting composition to be subjected to bulk polymerization which comprises the pigment, the polymerizable monomer and optionally the resin may be effected with the aid of a conventional dispersing machine such as a roll mill, a colloid mill, a fluid energy dispersing machine, an oscillation ball mill, a ball mill or a sand grinding mill. The conditions for the dispersion are not particularly different from those adopted in the case of conventional solution type paints, and may be appropriately chosen depending on the kind of the dispersing machine and degree of dispersion required. In the case where polymerization of the contained polymerizable monomers during the dispersing treatment is not desired, a conventional polymerization inhibitor such as hydroquinone or 2,2'-diphenyl-1-picrylhydrazide may be employed.

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The product obtained by the bulk polymerization is then, as such or after the addition of further polymerizable monomers, dispersed in water in the presence of a suspension stabilizer by a conventional procedure such as stirring.

As the suspending agent, there may be exemplified a natural high polymer or its derivative (e.g. gelatine, tragacanth, starch, methylcellulose, hydroxypropylcellulose, hydroxypropylmethylcellulose or carboxymethylcellulose), a vinyl alcohol copolymer (e.g. polyvinyl alcohol or partially saponified polyvinyl alcohol), a synthetic high polymer (e.g. polyacrylic acid salt, polymethacrylic acid salt or polyacrylamide), a hardly soluble salt (e.g.  $\text{BaSO}_4$ ,  $\text{CaSO}_4$ ,  $\text{BaCO}_3$ ,  $\text{CaCO}_3$ ,  $\text{MgCO}_3$  or  $\text{Ca}_3(\text{PO}_4)_2$ ), an inorganic high polymer (e.g. talc, bentonite, silicic acid, diatomaceous earth or clay), a metal powder or a metal oxide powder. As the stabilization promoter, a salt such as  $\text{NaCl}$ ,  $\text{KCl}$  or  $\text{Na}_2\text{SO}_4$ , a surface-active agent or the like may be employed.

The product obtained by the bulk polymerization may be alternatively emulsified in water in the presence of an emulsifier by a similar procedure. As the emulsifier, there may be exemplified an anionic surface-active agent (e.g. alkyl or alkylaryl sulfonic or sulfuric acid salt or salt of dialkylsulfosuccinate), a non-ionic surface-active agent (e.g. fatty acid ester or ether of polyoxyethylene), a high polymer emulsifier (e.g. a water-soluble high polymer), etc. As the stabilization promoter, a cellulose derivative such as hydroxyethylcellulose or the like is used. Two or more kinds of these agents may be used at the same time. Further, alternatively, the product of the bulk polymerization may be dispersed in water in the presence of a salt (e.g. amine salt) or an ethylenic monocarboxylic acid such as acrylic acid or methacrylic acid and, if necessary, another polymerizable monomer. Furthermore, the product of the bulk polymerization may be dispersed in water by using a system obtained by neutralization of a polymer of polycarboxylic acid with a base such as an amine, or directly by neutralizing the product with a base when the product itself contains a carboxyl group.

The bulk polymerization and the suspension or emulsion polymerization of the invention may be carried out in the presence of a conventional catalyst. Examples of such catalyst are an organic peroxide (e.g. benzoyl peroxide or lauroyl peroxide), an inorganic peroxide (e.g. potassium peroxide, ammonium peroxide, hydrogen peroxide or sodium peroxide) or an azo compound (e.g. azobisisobutyronitrile, to 2,2'-azobis-2,4-dimethylvaleronitrile). There may also be employed a redox catalyst comprising a

combination of an oxide with a reducing agent such as potassium pyrosulfite, sodium hydrogensulfite or triethanolamine. The catalyst for the suspension or emulsion polymerization may be previously incorporated insofar as the bulk polymerization can be controlled. In either one of the bulk polymerization and the suspension or emulsion polymerization or both of them, there may be further employed a conventional chain transfer agent such as a primary or tertiary dodecylmercaptan, a disulfide (e.g. diisopropyl-xanthogendisulfide) or a halide, various additives conventionally employed for the production of paints and inks such as a wetting agent, a flowing agent, a hardening catalyst, an antioxidant or a plasticizer and a crosslinking agent. As regards the use of a crosslinking agent, sufficient care should be taken to prevent undesirable side reactions such as crosslinking as mentioned above. There may also be employed an organic solvent having a boiling point of approximately 60 to 140°C or a small amount of water (i.e. not more than 5% by weight preferably less than 1%) so as to control the reaction heat at the bulk polymerization state. Where water is used it is present in the vapour phase above the reaction mixture in the liquid phase and acts to suppress rises in the temperature of the reaction mixture.

In carrying out the bulk polymerization, the composition may stick to the inner wall of the reaction vessel, and cleaning of the thus contaminated reaction vessel is sometimes difficult. In such cases, a water-soluble high polymer (e.g. a natural high polymer or its derivative such as methylcellulose or methoxycellulose, a water-soluble vinyl compound such as polyvinyl alcohol or polyacrylic acid) chosen from the said suspension stabilizers or emulsifiers is, as such or in the form of a solution or dispersion, applied to the inner wall of the reaction vessel and, if necessary, subjected to drying prior to the bulk polymerization. By such treatment, sticking of the composition to the inner wall of the reaction vessel can be minimized. Besides, the water-soluble high polymer used is dissolved out into the aqueous phase satisfactorily at the subsequent suspension or emulsion polymerization stage and serves as the stabilizing agent without hindering the preparation of the desired pigment dispersed composition.

The bulk polymerization of the invention is usually carried out at a temperature within the range of from about 60°C to 160°C inclusive, preferably within the range of from about 80°C. to 140°C for a duration of time of about 1 to 20 hours, preferably from about 1 to 15 hours, so as to attain such a conversion as effecting smoothly the sub-

sequent suspension or emulsion polymerisation, usually of from about 10 to 100%, preferably from about 30 to 90%. The suspension polymerization is usually effected at a temperature within the range of from about 50°C to 100°C, inclusive, preferably from about 60°C. to 90°C. for about 3 to 20 hours, preferably from 4 to 15 hours. The emulsion polymerization is carried out usually at a temperature within the range of from 0°C to 100°C, preferably from about 30°C. to 90°C, for about 1 to 10 hours.

By observation of the solid components in the pigment dispersed composition as prepared above using a scanning electron microscope, it is confirmed that, for instance in case of the pigment being titanium white, particles of 1  $\mu$  or less (usually 0.1 to 0.5  $\mu$ ) in particle size are present in a dispersed state without substantial coagulation between them, which shows that the pigment-dispersion composition of the invention can be utilized advantageously as a coating composition such as a powdery paint or a slurry paint.

For use as a powdery coating composition, the solid components are collected from the pigment-dispersed composition by a conventional separation procedure, washed with water and dried. If desired, a pulverization operation may be applied to the solid components at any stage, for instance, before collection or after drying. For use as a slurry coating composition, the pigment dispersed composition may be employed as such but is preferably pulverized at least in the wet state. The solid content in the slurry coating composition can be adjusted by adding an appropriate amount of water thereto or eliminating a suitable amount of water therefrom before and/or after the pulverization. The pulverization in a wet state, for instance, in the form of an aqueous suspension is advantageous in ensuring a sufficient wetting of the solid components with water, and achieving a finer minimization of the solid particles avoiding the production of dust and noise. The coating film formed by the use of a pigment-dispersed composition wherein the solid components are pulverized as above shows a better smoothness and gloss.

The present invention will be hereinafter explained further in detail with reference to the following Examples and Comparative Examples wherein all parts are by weight.

The mercapto group-containing alkyd resin employed in these examples is that prepared by subjecting a mixture of neopentyl glycol (69.4 parts), trimethylolpropane (33.4 parts), isophthalic acid (119.7 parts) and adipic acid (13.2 parts) to polycondensation at a temperature within the range of from 180°C to 220°C, cooling the reaction mixture to a temperature below 150°C.

adding thiglycollic acid (16.6 parts) to the reaction system and then effecting again the polycondensation at a temperature within the range of from 180°C to 200°C, and having the following physical properties: acid value, 10 or less; viscosity (involatile components, 60% by weight; Gardner bubble viscometer), L - R; number average molecular weight, 1800; weight average molecular weight, 4500.

#### Example 1

An acrylic copolymer (5.3 parts), prepared by subjecting a mixture of the mercapto group-containing alkyd resin, methyl methacrylate, styrene, *n*-butyl methacrylate and glycidyl methacrylate in a weight proportion of 10 : 38 : 19 : 10 : 23 to suspension polymerization in the presence of 2,2'-azobis-2,4-dimethylvaleronitrile as a polymerization initiator and *t*-dodecylmercaptan as a chain transfer agent at 70°C for 5 hours, is admixed with methyl methacrylate (7.35 parts), styrene (3.67 parts), *n*-butyl methacrylate (1.93 parts) and glycidyl methacrylate (4.45 parts) to yield a liquid composition (22.7 parts).

To the resulting liquid composition, titanium white ("Ti-Pure R-900" (trade mark) manufactured by DuPont) (25 parts) is added and thoroughly dispersed with the aid of a sand grinding mill until the particle size of the pigment becomes 10  $\mu$  or less. Then, the mixture is admixed with *t*-dodecylmercaptan (0.3 part) and placed in a flask to whose inner wall has been previously applied a 2% aqueous solution of methylcellulose dried at 120 to 130°C for about 1 hour. The temperature is raised from the room temperature to 90°C in 15 minutes while stirring, and a mixture of the liquid composition (47.7 parts), azobisisobutyronitrile (0.43 part) and *t*-dodecylmercaptan (0.3 part) is added dropwise in the space of 1 hour. On beginning the addition, the temperature is raised from 90°C up to 120°C, and the same temperature is maintained until the completion of the addition so as to effect bulk polymerization. Conversion: 80 to 90%.

After completion of the addition, the mixture is gradually cooled with stirring for about 30 minutes. Then, *n*-butyl methacrylate (10.4 parts) is added thereto at a temperature not higher than 140°C, styrene (19.8 parts) is added at a temperature not higher than 100°C and methyl methacrylate (42.4 parts), glycidyl methacrylate (24.0 parts) and 1,10-decanedicarboxylic acid (23.0 parts) are added at 50 to 60°C with sufficient stirring. *t*-Dodecylmercaptan (1.33 parts) and 2,2'-azobis-2,4-dimethylvaleronitrile (2.12 parts) are incorporated into the resulting dispersed composition.

Then, a 0.5% aqueous solution of methyl-

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cellulose (600 parts) is charged into the same flask to initiate suspension polymerization. After the reaction has been carried out at 70°C, for 5 hours, the reaction mixture is filtered, and the residue is washed with water and dried to yield a pigment-dispersed composition as beads of 0.1 to 1.0 mm in particle size.

The resulting pigment dispersed composition is, after pulverization and passage through a 200 mesh sieve, applied to a polished steel plate by electrostatic coating and baked at 180°C for 10 minutes. At the baking stage, the composition shows an excellent fluidity to afford a smooth and lustrous coating film. The coating film is then peeled off, and its sectional observation is effected with the aid of a scanning electron microscope, wherein it is confirmed that particles of 0.1 to 0.5  $\mu$  in particle size which are considered to be the primary particles of the pigment are uniformly dispersed without coagulation.

#### Example 2

To the liquid composition obtained in Example 1 (22 parts), titanium white as used in Example 1 (40 parts) is added and well dispersed with the aid of a sand grinding mill until the particle size of the pigment becomes 10  $\mu$  or less. After the addition of *t*-dodecylmercaptan (0.8 part), the mixture is charged into a flask, and a mixture of the liquid composition obtained in Example 1 (9.42 parts), azobisisobutyronitrile (0.2 part) and *t*-dodecylmercaptan (0.4 part) is added dropwise thereto to effect bulk polymerization as in Example 1 (Conversion: 85%).

The reaction mixture is then gradually cooled with stirring, and *n*-butyl methacrylate (8.4 parts) and styrene (16.1 parts) are added thereto as in Example 1. Then a mixture comprising methyl methacrylate (23.7 parts), glycidyl methacrylate (14.4 parts), 1,10-decanedicarboxylic acid (14.0 parts) and polysiloxane (0.29 part) is further added with sufficient stirring. *t*-Dodecylmercaptan (2.24 parts) and 2,2'-azobis-2,4-dimethylvaleronitrile (2.53 parts) are incorporated into the resulting dispersed composition.

Then a 0.5% aqueous solution of methylcellulose (300 parts) is charged into the same flask to initiate suspension polymerization. After the reaction has been carried out at 70°C for 5 hours, the reaction mixture is filtered, and the residue is washed with water and dried to yield a pigment dispersed composition as beads of 0.1 to 1.0 mm in particle size.

The resulting pigment-dispersed composition is, after pulverization and passage through a 200 mesh sieve, applied to polished steel by electrostatic coating and baked at 180°C for 20 minutes. At the

baking stage, the composition shows a sufficient fluidity to yield a smooth and lustrous coating film. The coating film is then peeled off, and its sectional observation is effected with the aid of a scanning electron microscope, whereby it is confirmed that particles of 0.1 to 0.5  $\mu$  in particle size which are considered to be the primary particles of the pigment are uniformly dispersed without coagulation. When the coating film is subjected to Erichsen's extruding test and to DuPont's impact test, values of 6 mm or more and of 30 cm are obtained, respectively. Thus, the presence of sufficient cross-linking is confirmed.

#### Comparative Example 1

To the liquid composition obtained in Example 1 (22 parts), titanium white as used in Example 1 (40 parts) is added and dispersed well by the aid of a sand grinding mill until the particle size of the pigment becomes 10  $\mu$  or less. Then, the acrylic copolymer as used in Example 1 (31.4 parts), *n*-butyl methacrylate (4.2 parts), styrene (8.2 parts), methyl methacrylate (11.8 parts), glycidyl-methacrylate (7.2 parts), *t*-dodecylmercaptan (2.24 parts), 2,2'-azobis-2,4-dimethylvaleronitrile (2.53 parts), 1,10-decanedicarboxylic acid (14.0 parts) and polysiloxane (0.29 part) are added thereto, and the resulting mixture is placed in a flask. A 0.5% aqueous solution of methylcellulose (300 parts) is added thereto, and suspension polymerization is carried out at 70°C for 5 hours. The reaction mixture is filtered, and the residue is washed with water and dried to yield a pigment-dispersed composition comprising the same constituents as in Example 2. The resulting composition is, after pulverization, applied to a substrate and baked, whereby the fluidity is not satisfactory. By the sectional observation of the formed coating film with the aid of a scanning electron microscope, the presence of coagulated pigment of 10  $\mu$  or more in size is confirmed.

#### Example 3

A mixture comprising the mercapto group-containing alkyd resin (1.50 parts), methyl methacrylate (7.95 parts), styrene (2.95 parts), *n*-butyl methacrylate (1.50 parts), glycidyl methacrylate (4.83 parts) and titanium white as used in Example 1 (25 parts) is dispersed well by the aid of a sand grinding mill until the particle size of the pigment becomes 10  $\mu$  or less.

The resulting composition is admixed with *t*-dodecylmercaptan (0.80 part) and placed in a flask. A mixture comprising methyl methacrylate (4.00 parts), styrene (1.48 parts), *n*-butyl methacrylate (0.75 part), glycidyl methacrylate (2.43 parts), azobisisobutyronitrile (0.2 part) and *t*-dodecylmercaptan (0.4 part) is added drop-

wise thereto in 1 hour to effect bulk polymerization as in Example 1. Conversion: 80 to 90%.

After completion of the addition, *n*-butyl methacrylate (4.72 parts), styrene (8.97 parts), methyl methacrylate (17.8 parts), glycidyl methacrylate (10.8 parts) and 1,10-decanedicarboxylic acid (14.0 parts) are added under sufficient stirring as in Example 1. *t*-dodecylmercaptan (1.68 parts) and 2,2'-azobis-2,4-dimethylvalero-nitrile (1.90 parts) are incorporated in the resulting dispersed composition. Then, a 0.5% aqueous solution of methylcellulose (300 parts) is added thereto, and suspension polymerization is effected at 70°C for 5 hours. The reaction mixture is filtered, and the residue is washed with water and dried to yield a pigment-dispersed composition as beads of 0.1 to 1.0 mm in particle size. The resulting composition is, after pulverization, applied to a substrate and baked. The composition shows an excellent fluidity at the baking stage to afford a smooth and lustrous coating film, which is peeled off, and its sectional observation is effected with the aid of a scanning electron microscope, whereby it is confirmed that particles of 0.1 to 0.5  $\mu$  in particle size, which are considered to be the primary particles of the pigment, are uniformly dispersed without coagulation.

#### Example 4

A mixture comprising methyl methacrylate (12.7 parts), *n*-butyl methacrylate (3.3 parts), styrene (6.3 parts), glycidyl methacrylate (7.7 parts) and Cingus Red B (manufactured by DuPont) (10 parts) is dispersed well by the aid of a sand grinding mill until the particle size of the pigment becomes 10  $\mu$  or less.

The resulting composition is admixed with *t*-dodecylmercaptan (0.5 part) and placed in a flask. The temperature is raised to 90°C, and a mixture comprising methyl methacrylate (8.46 parts), *n*-butyl methacrylate (2.20 parts), styrene (4.20 parts), glycidyl methacrylate (5.13 parts), *t*-dodecylmercaptan (0.33 part) and azobisisobutyronitrile (2.0 parts) is added dropwise to effect bulk polymerization as in Example 1. (Conversion: 75 to 80%).

After completion of the addition, the temperature is lowered to room temperature, and the methyl methacrylate (21.2 parts), *n*-butyl methacrylate (5.5 parts), styrene (10.5 parts), glycidyl methacrylate (12.8 parts), 1,10-decanedicarboxylic acid (15.0 parts), *t*-dodecylmercaptan (1.50 parts) and 2,2'-azobis-2,4-dimethylvaleronitrile (2.0 parts) are added thereto. Then, a 0.5% aqueous solution of methylcellulose (300 parts) is further added to initiate suspension polymerization. After the reaction has been carried out at 70°C for

5 hours, the reaction mixture is filtered, and the residue is washed with water and dried to yield a pigment-dispersed composition as beads of 0.1 to 0.5 mm in particle size.

The thus prepared pigment-dispersed composition is pulverized and applied to a substrate as in Example 1, whereby a smooth and lustrous coating film is obtained. By the sectional observation of the coating film with the aid of a scanning electron microscope, it is confirmed that particles of 0.1 to 0.5  $\mu$  in particle size, which are considered to be the primary particles of the pigment, are uniformly dispersed without coagulation.

#### Example 5

To a liquid composition comprising the mercapto group-containing alkyd resin (1.52 parts), isobutyl methacrylate (1.52 parts), styrene (2.90 parts), methyl methacrylate (4.00 parts) and 2-hydroxyethyl acrylate (9.4 parts), titanium white as used in Example 1 (30.0 parts) is added and dispersed well by the aid of a sand grinding mill until the particle size of the pigment becomes 10  $\mu$  or less. The resulting mixture is admixed with *t*-dodecylmercaptan (0.8 part) and placed in a flask. The temperature is raised as in Example 1, and a mixture comprising the liquid composition (9.67 parts), azobisisobutyronitrile (0.2 part) and *t*-dodecylmercaptan (0.4 part) is added dropwise to effect bulk polymerization as in Example 1 (Conversion: 80 to 90%).

After completion of the addition, the mixture is cooled gradually while stirring, and methyl methacrylate (21.55 parts), styrene (9.35 parts), isobutyl methacrylate (3.57 parts), *n*-butyl acrylate (2.01 parts) and a blocked polyisocyanate (32.0 parts) are added thereto under sufficient stirring. *t*-dodecylmercaptan (1.50 parts) and 2,2'-azobis-2,4-dimethylvaleronitrile (2.00 parts) are incorporated into the resulting dispersed composition. A 0.5% aqueous solution of methylcellulose (300 parts) is then charged into the same flask to effect suspension polymerization as in Example 1. The reaction mixture is filtered, and the residue is washed and dried.

The resulting pigment-dispersed composition is pulverized and applied to a substrate as in Example 1, whereby a smooth and lustrous coating film is obtained. By the sectional observation of the coating film as in Example 1, the absence of coagulation in the pigment is confirmed. The hydroxyl value of the composition is determined to be 98.5% of the theoretical value, which shows that movement into the aqueous phase has hardly occurred.

#### Comparative Example 2

To a liquid composition comprising the mercapto group-containing alkyd resin (2.28 parts), methyl methacrylate (30.5 parts),

- isobutyl methacrylate (6.5 parts), *n*-butyl acrylate (2.2 parts), styrene (15.2 parts) and 2-hydroxyethyl acrylate (15.6 parts), titanium white as used in Example 1 (30 parts) is added and dispersed well by the aid of a sand grinding mill until the particle size of the pigment becomes 10  $\mu$  or less. The resulting mixture is admixed with *t*-dodecylmercaptan (2.1 parts) and 2,2'-azobis-2,4-dimethylvaleronitrile (2.8 parts) under stirring to yield a uniform mixture, which is placed in a flask. Then, a solution of methylcellulose (300 parts) is added thereto to effect suspension polymerization as in Example 1. After the reaction, the reaction mixture is filtered, and the residue is washed and dried. The hydroxyl value of the thus prepared composition is determined to be 53.5% of the theoretical value.
- Example 6**  
Cellulose acetate butyrate ("EAB-451-1" manufactured by Eastman Kodak) (18 parts) is dissolved in a mixture of methyl methacrylate (30 parts) and *n*-butyl acrylate (20 parts), and titanium white ("Tipake R-820" (trade mark) manufactured by Ishihara Sangyo) (60 parts) is added thereto and well dispersed with the aid of a ball mill until the particle size of the pigment becomes 10  $\mu$  or less. The resulting dispersed composition (66 parts) is admixed with *t*-dodecylmercaptan (0.8 part) and placed in a flask. A dissolved mixture comprising the rest of the dispersed composition (62 parts), *t*-dodecylmercaptan (0.4 part) and azobisisobutyronitrile (0.2 part) is added dropwise thereto while stirring to effect bulk polymerization as in Example 1.
- Methyl methacrylate (20 parts), styrene (25 parts) and isobutyl methacrylate (12 parts) are added to the polymerization product while cooling gradually, and 2,2'-azobis-2,4-dimethylvaleronitrile (4.0 parts) is further added to make a uniform solution, which is charged into another flask containing a 1.5% aqueous dispersion of BaSO<sub>4</sub> (700 parts). The contents are stirred to obtain an aqueous dispersion, and suspension polymerization is carried out. After the reaction, the reaction mixture is filtered, and the residue is washed and dried.
- The resulting pigment-dispersed composition is, after pulverization as in Example 1, applied to a substrate and baked at 200°C. for 30 minutes. The composition shows an excellent fluidity to afford a smooth and lustrous coating film, which is peeled off, and its sectional observation is effected as in Example 1, whereby it is confirmed that particles of 0.1 to 0.5  $\mu$  in particle size which are considered to be the primary particles of the pigment are uniformly dispersed without coagulation.
- Example 7**  
The mercapto group-containing alkyd resin (32 parts) is dissolved in a mixture of methyl methacrylate (22.4 parts), styrene (25.6 parts) and acrylic acid (8.4 parts), and titanium white as used in Example 1 (150 parts) is added thereto and dispersed well with the aid of a sand grinding mill until the particle size of the pigment becomes 10  $\mu$  or less. The thus obtained dispersed composition is admixed with *t*-dodecylmercaptan (1.8 parts) and placed in a flask. Then, a dissolved mixture comprising methyl methacrylate (22.4 parts), styrene (25.6 parts), acrylic acid (8.4 parts), *t*-dodecylmercaptan (1.8 parts) and azobisisobutyronitrile (3.6 parts) is added dropwise thereto as in Example 1 under reflux in the stream of nitrogen gas. After completion of the addition, the mixture is kept at 130 to 140 °C for 20 hours (conversion: 90%).
- The polymerization product is cooled gradually, and methyl methacrylate (64 parts), styrene (64 parts) and *n*-butyl methacrylate (32 parts) are added thereto under stirring. A part of the resulting uniform mixture (300 parts) is admixed with dimethylethanolamine (7.2 parts) under stirring, and ammonium persulfate (1.66 parts) and water (600 parts) are further added. The resulting mixture is added dropwise to another flask containing water (340 parts) at 60 to 90 °C in 2.5 hours. After completion of the addition, the reaction is continued at about 90°C for 3 to 4 hours to obtain a stable aqueous dispersion containing 43% by weight of non-volatile components.
- The resulting aqueous dispersion is applied to an iron plate and baked at 80°C. for 30 minutes, whereby a smooth and lustrous coating film is obtained. By the sectional observation of the coating film as in Example 1, it is confirmed that particles of the pigments having a particle size of 0.1 to 0.5  $\mu$  are uniformly dispersed without coagulation.
- Example 8**  
A mixture comprising the mercapto group-containing alkyd resin (1.5 parts), methyl methacrylate (7.95 parts), styrene (2.95 parts), *n*-butyl methacrylate (1.5 parts), glycidyl methacrylate (4.83 parts) and titanium white as used in Example 1 (25 parts) is dispersed well by the aid of a sand grinding mill until the particle size of the pigment becomes 10  $\mu$  or less.
- The resulting composition is admixed with *t*-dodecylmercaptan (0.80 part) and placed in a flask. The temperature is raised from room temperature to 90°C in 15 minutes under stirring, and a mixture comprising methyl methacrylate (4 parts), styrene (1.48 parts), *n*-butyl methacrylate (0.75 part), glycidyl methacrylate (2.43 parts), azobisisobutyronitrile (0.2 part) and *t*-dodecylmercaptan (0.4 part) is added



dropwise thereto in 1 hour while keeping the temperature between 110 and 120°C, whereby bulk polymerization is effected. (conversion: 80 to 90%).

- 5 The reaction mixture is cooled, and *n*-butyl methacrylate (4.72 parts), styrene (8.97 parts), methyl methacrylate (17.8 parts), glycidyl methacrylate (10.8 parts) and 1,10-decanedicarboxylic acid (13.1 parts) are added thereto under stirring. Then, *t*-dodecylmercaptan (1.68 parts) and 2,2'-azobis-2,4-dimethylvaleronitrile (1.9 parts) are admixed with the resulting mixture, a 0.5% aqueous solution of methylcellulose (300 parts) is added thereto, and suspension polymerization is carried out at 70°C. for 5 hours.

The resulting aqueous dispersion is washed with water, and the washed dispersion comprising the solid components and water in a weight proportion of 1 : 1 is charged in a ball mill, followed by pulverization for 20 hours. The pulverized product (non-volatile components, 33% by weight) is passed through a 200 mesh sieve to yield a slurry composition for coating).

The slurry composition is applied to a zinc phosphated iron plate by air-spraying and baked at 180°C for 20 minutes, whereby a smooth and lustrous coating film is formed.

#### WHAT WE CLAIM IS:

1. A process for preparing a pigment-dispersed composition, wherein a liquid composition comprising at least one ethylenically unsaturated, polymerizable liquid monomer and at least one pigment in a particulate form dispersed therein in an amount of not more than 70% by weight of the pigment based on the weight of the liquid composition, is subjected to bulk polymerization without cross-linking in a substantially non-aqueous system at a temperature of from 60°C to 160°C and wherein, thereafter, the resulting reaction mixture optionally after the addition thereto of a further amount of the said liquid monomer or of at least one other ethylenically unsaturated, polymerizable liquid monomer is subjected either to suspension polymerization in an aqueous system at a temperature of from 50°C to 100°C or to emulsion polymerization in an aqueous system at a temperature of 0°C to 100 °C to obtain a dispersion of the pigment particles in the polymer particles produced from the liquid monomer or monomers.

2. A process according to claim 1, wherein the liquid composition further comprises at least one resin dissolved or dispersed in the liquid monomer.

3. A process according to claim 2, wherein the resin has an active group, on which the liquid monomer is grafted.

4. A process according to claim 3, wherein the active group is a mercapto

group.

5. A process according to claim 4, wherein the mercapto group has been introduced into the resin by reaction between a hydroxyl group and a mercaptocarboxylic acid.

6. A process according to claim 5, wherein the mercaptocarboxylic acid is thioglycollic acid.

7. A process according to claim 3, wherein the active group is an ethylenically unsaturated group.

8. A process according to claim 3, wherein the active group is a group having a C-H bond of which the hydrogen atom can be abstracted by a free radical.

9. A process according to any of claims 1 to 8, wherein the liquid monomer consists of a monovinyl aromatic hydrocarbon, an ethylenically unsaturated carboxylic acid, an ethylenically unsaturated carboxylic acid ester, acrylonitrile, methacrylonitrile, a glycidyl vinyl compound, an ethylenically unsaturated compound having at least one hydroxyl group, an ethylenically unsaturated amide or an ethylenically unsaturated compound having at least one blocked isocyanate group, or any mixture thereof.

10. A process according to any of claims 1 to 11, wherein the pigment is a mixture of two or more pigments.

11. A process according to claim 10, wherein the liquid composition is colour matched prior to the bulk polymerization.

12. A process according to any of claims 2 to 11, wherein the resin is used in an amount within the range of 1 to 60% inclusive, by weight, based on the weight of the liquid composition.

13. A process according to any of claims 1 to 12, wherein the bulk polymerization is carried out in a reaction vessel having a wall onto which a suspending agent is applied.

14. A process according to claim 13, wherein the suspending agent is a water-soluble high polymer.

15. A process according to any of claims 1 to 14, in which the solid components are collected from the reaction mixture after the suspension or emulsion polymerization.

16. A process according to claim 15, wherein the collected solid components are washed with water and dried.

17. A process according to claim 15 or 16, wherein the solid components are pulverized.

18. A process according to claim 17, wherein the pulverization is carried out on the solid components in a wet state.

19. A process according to claim 1 substantially as herein described with reference to any of the specific Examples.

20. A pigment-dispersed composition prepared by a process as claimed in any of claims 1 to 19.

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| 5 | 21. A powdery coating composition prepared by a process as claimed in any of claims 15 to 18.<br>22. A slurry coating composition prepared by a process as claimed in any of claims 15 to 18. | Elkington and Fife<br>Chartered Patent Agents<br>52-54 High Holborn<br>London WC1V 6SH | 10 |
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